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MEASUREMENTS OF RECOMBINATION
OF ELECTRONS WITH HCO⁺ IONS

BY

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Electrons with HCO⁺ Ions

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Abstract

Recombination coefficients of electrons with HCO⁺ ions have been determined with a microwave afterglow/mass spectrometer apparatus. Afterglow measurements of electron density decays in neon-hydrogen-carbon monoxide mixtures are correlated with the decay of mass-identified ion currents to the wall of the microwave cavity. At the appropriate partial pressures of hydrogen and carbon monoxide in the mixture, the ion HCO⁺ dominates the ion composition and its wall current approximately "tracks" the electron density decay curve. From recombination controlled electron density decay curves, the values $\alpha(\text{HCO}^+) = (3.3 \pm 0.5)$ and $(2.0 \pm 0.3) \times 10^{-7} \text{ cm}^3/\text{sec}$ are obtained at 205 and 300 K, respectively. The implications of these results for models of polyatomic molecule formation in dense interstellar clouds are briefly discussed.

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I. Introduction

The interest in the recombination rate for the HCO^+ ion stems from its importance in flame studies, as an interstellar molecular ion, and possibly as an ionospheric ion in the atmospheres of the earth and outer planets. In the first instance chemionization of CH radicals and oxygen atoms in flames by the associative ionization reaction,



produces HCO^+ ions which may either react further with the other neutral species such as H_2O or may recombine dissociatively with electrons according to the reaction,



other branches of reaction (2) resulting in formation of C + OH and O + CH may also occur.

Secondly, Buhl and Snyder⁽²⁾, using a radio telescope, detected a microwave line of transition frequency 89, 190 MHz in a few radio sources such as Orion. They were not able to make a positive spectral identification of this line, referring to it as the X-ogen line (i.e. of unknown, extraterrestrial origin). Klemperer⁽³⁾ has suggested the molecular ion HCO^+ as the source of this radio line and in a model of the formation of polyatomic molecules in dense, interstellar clouds⁽⁴⁾ has suggested that the ion is formed from H_3^+ by the fast rearrangement reaction



which has a rate coefficient $k = 1.4 \times 10^{-9} \text{ cm}^3/\text{sec}$ at 300 K.⁽⁵⁾

Inasmuch as one of the important removal processes for the HCO⁺ ion both in flames and in the interstellar clouds may be dissociative recombination, we have undertaken measurements of the recombination coefficient, $\alpha(\text{HCO}^+)$, at 205 and 300 K.

II. Apparatus

We have applied our microwave afterglow/mass spectrometer apparatus to the determination of the recombination coefficient of electrons with HCO⁺ ions (see the preceding paper and the cited references for a more detailed description of the apparatus).^(6,7,8) Gas mixtures of research grade neon, hydrogen and carbon monoxide are admitted to a microwave resonant cavity and ionized by a 40 μsec pulse of microwave energy repeated ten times per second. The electron density as a function of time during the afterglow is determined from measurements of the resonant frequency shift of the cavity.⁽⁹⁾ The afterglow ions which diffuse to the wall and effuse through a small hole are mass identified by a differentially pumped quadrupole mass spectrometer. The ion wall currents as a function of time provides a measure of the decay of ion concentrations during the afterglow.

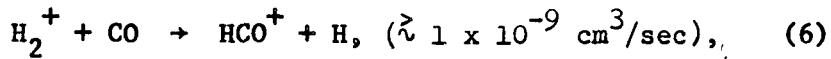
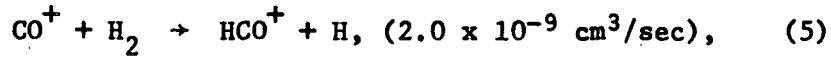
III. Measurements and Discussion

By adjusting the gas mixture and ionizing pulse width we can obtain conditions in which afterglow ionization processes are unimportant, electron-ion recombination is the dominant loss process and a single positive-ion species predominates. Assuming that negative ions

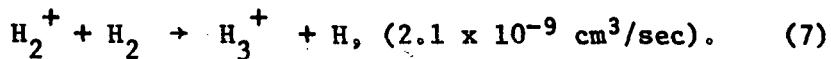
concentrations are negligible, the decay of electron density n_e is given approximately by^(7,8)

$$1/n_e(t) \approx 1/n_e(0) + \alpha t, \quad (4)$$

where α is the recombination coefficient. The microwave cavity measurements provide microwave-field averaged values of the electron density, $\bar{n}_{\mu\omega}(t)$. In order to obtain values of α from the slopes of $1/\bar{n}_{\mu\omega}(t)$ vs. time curves, correction factors⁽¹⁰⁾ are used which take into account ambipolar diffusion effects on the electron spatial distribution within the cavity. The principal steps in the formation of HCO^+ ions in hydrogen-carbon monoxide-neon mixtures are rather complicated. The first step is Penning ionization of H_2 and CO by neon metastable atoms. The H_2^+ and CO^+ ions then undergo fast two-body rearrangement reactions^(11,12,13)



and



The H_3^+ ions are converted to HCO^+ by reaction (3). As may be seen from the data in Fig. (1b), the ions CO^+ , H_2^+ , and H_3^+ disappear quickly in the afterglow and HCO^+ rapidly becomes the principal ion. The decay of the HCO^+ ion wall current follows the electron density decay curve quite well during the later afterglow. Unfortunately a small concentration of the rather serious impurity ion H_3O^+ appears, possibly formed by the reaction,⁽¹⁴⁾



Even though we have inserted a refrigerated (77 K) zeolite trap in the gas supply lines to aid in further gas purification, the ion wall current of H_3O^+ remains at a level of approximately a few percent of the HCO^+ ion current during the recombination controlled afterglow. The corrected slope in the plot of $1/\bar{n}_{\mu W}$ vs. t yields the apparent recombination coefficient $\alpha_a = 2.5 \times 10^{-7} \text{ cm}^3/\text{sec}$. After correcting for the presence of the H_3O^+ ions⁽⁷⁾ by using $\alpha(\text{H}_3\text{O}^+) = 1.3 \times 10^{-6} \text{ cm}^3/\text{sec}$ at 300 K and an average ratio $[\text{H}_3\text{O}^+]/[\text{HCO}^+] = 0.04$, a value $\alpha(\text{HCO}^+) = 2.0 \times 10^{-7} \text{ cm}^3/\text{sec}$ is obtained at 300 K.

Similar data obtained at 205 K are shown in Fig. (2). The HCO^+ ion wall current is seen to "track" the electron density decay curve. At this lower temperature, the wall current of the impurity ion H_3O^+ is much smaller than that of the ion HCO^+ . The corrected slope in Fig. (2a) yields the apparent recombination coefficient $\alpha_a = 3.5 \times 10^{-7} \text{ cm}^3/\text{sec}$. By using the estimated value $\alpha(\text{H}_3\text{O}^+) = 1.6 \times 10^{-6} \text{ cm}^3/\text{sec}$ at 205 K⁽⁷⁾ and taking the ratio of ion densities $[\text{H}_3\text{O}^+]/[\text{HCO}^+] \sim 10^{-2}$, the apparent recombination coefficient is corrected to yield the value $\alpha(\text{HCO}^+) = 3.3 \times 10^{-7} \text{ cm}^3/\text{sec}$ at 205 K.

Other measurements in which $P(\text{H}_2)$ and $P(\text{CO})$ were varied over the range 0.6 - 1.3 mTorr and $P(\text{Ne})$ over the range 4.6 - 23 Torr gave values of $\alpha(\text{HCO}^+)$ in the range of $(3.1 - 3.5) \times 10^{-7} \text{ cm}^3/\text{sec}$ at 205 K. It was not possible to measure $\alpha(\text{HCO}^+)$ outside these pressure ranges because the HCO^+ ion was not dominant during the afterglow. Also, helium was used instead of neon as a buffer gas in the determination of $\alpha(\text{HCO}^+)$. Unfortunately in

this case the undesired ion C⁺ produced in the microwave discharge was comparable to the major ion HCO⁺ during the afterglow, precluding accurate determinations of $\alpha(\text{HCO}^+)$. However, the approximate values of $\alpha(\text{HCO}^+)$ deduced from the measurements using helium as a buffer gas are in good agreement with the results obtained using neon as a buffer gas.

As in previous studies^(6,7) the principal uncertainties in the recombination coefficient determinations arise from imperfect knowledge of the spatial distribution of the electrons in the cavity at the start of the afterglow and from the effects of the small concentration of impurity ions (in this case, H₃O⁺). Considering these uncertainties and the ranges of α values obtained, the assigned values are $\alpha(\text{HCO}^+) = (3.3 \pm 0.5) \times 10^{-7} \text{ cm}^3/\text{sec}$ and $(2.0 \pm 0.3) \times 10^{-7} \text{ cm}^3/\text{sec}$ at T = 205 K and T = 300 K, respectively.

The magnitude of the recombination coefficient for HCO⁺ ions deduced in the present studies, $\sim 10^{-7} \text{ cm}^3/\text{sec}$, is typical of the values found for many other simple molecular ions.⁽¹⁵⁾ However, over the limited temperature range studied, 205 to 300 K, the variation of α is somewhat stronger ($\sim T^{-1}$) than the $T^{-1/2}$ dependence predicted for the direct dissociative process at low temperatures. Similar $\sim T^{-1}$ temperature dependences have been noted for O₂⁺ ions⁽¹⁶⁾ and for NO⁺ ions⁽⁸⁾ at temperatures between 200 and 300 K. It has been suggested that this more rapid variation results from the indirect dissociative process.⁽¹⁷⁾

In order to apply the laboratory values of $\alpha(\text{HCO}^+)$ to models of polyatomic molecule formation in dense interstellar clouds it is necessary to extrapolate to temperatures of ~ 20 K. Using the T^{-1} dependence suggested by our measurements, a value in excess of $3 \times 10^{-6} \text{ cm}^3/\text{sec}$

would be expected under interstellar conditions, necessitating modification of current models⁽⁴⁾ of polyatomic molecule formation which have employed values in the 10^{-7} cm³/sec range.

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Figure Captions

- Fig. 1.** (a) "Recombination plot" of electron density decay at 300 K
(b) Comparison of electron density and ion wall current decays under condition where HCO^+ dominates the ion composition.
- Fig. 2.** (a) "Recombination plot" of electron density decay at 205 K.
(b) Comparison of electron density and ion wall current decay under condition where HCO^+ dominates the ion composition.

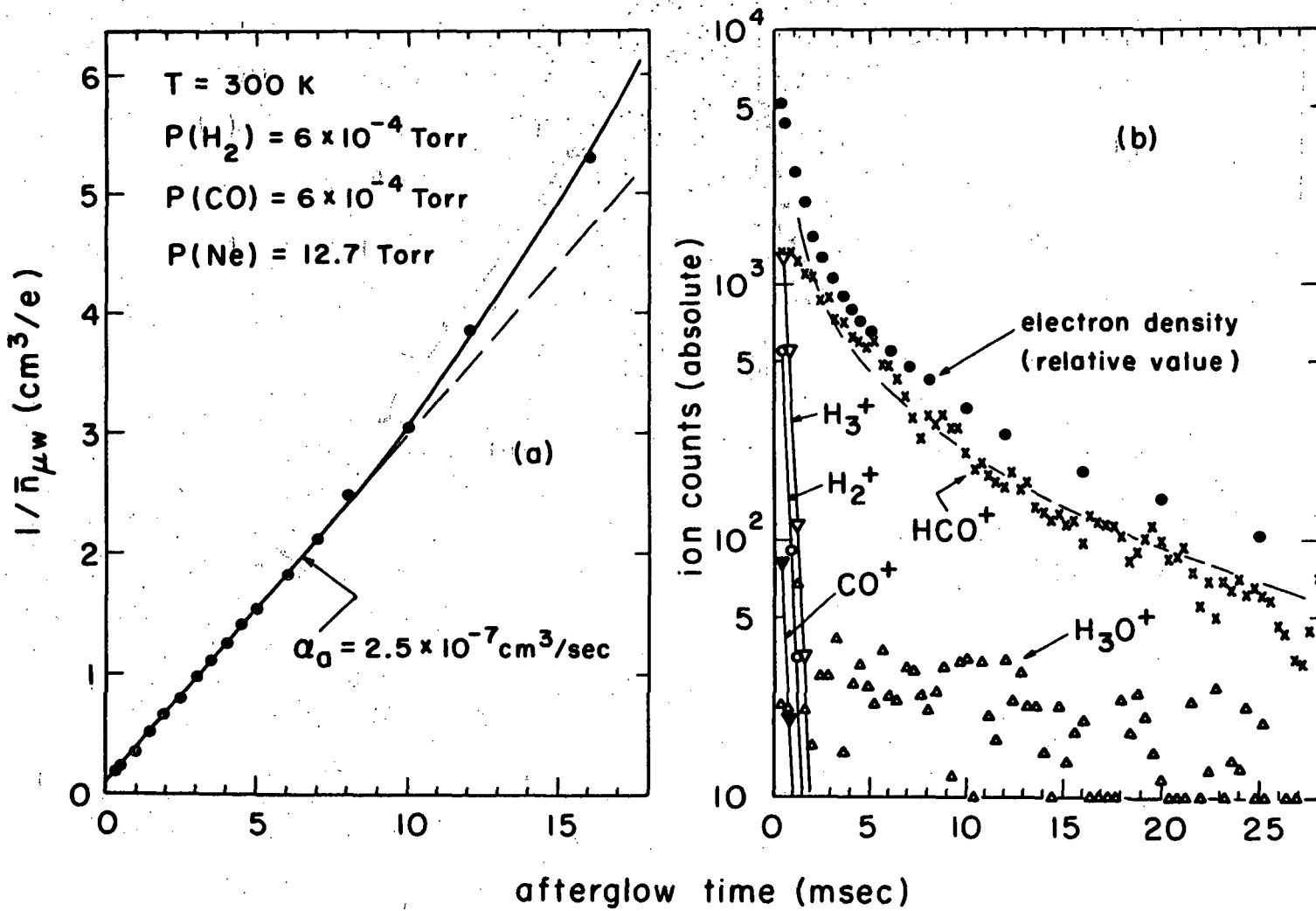


Figure 1

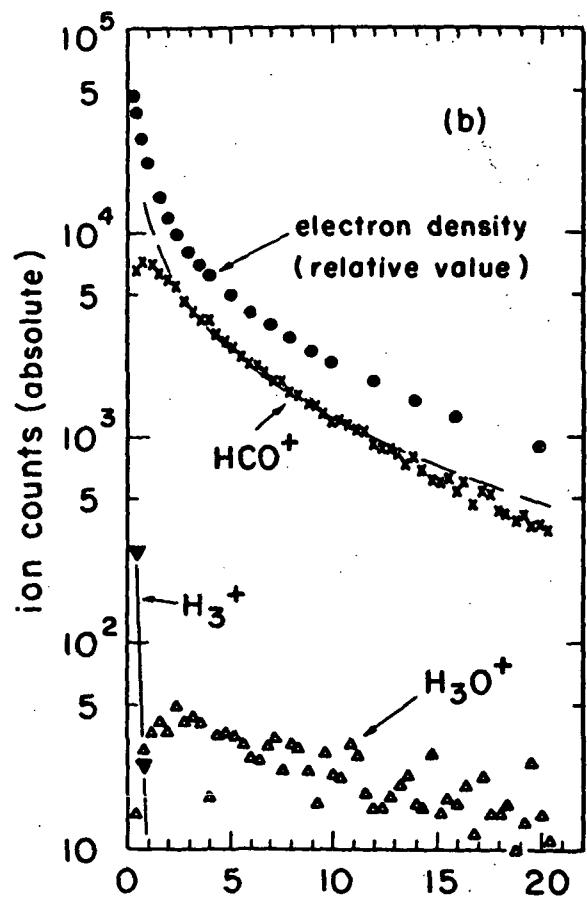
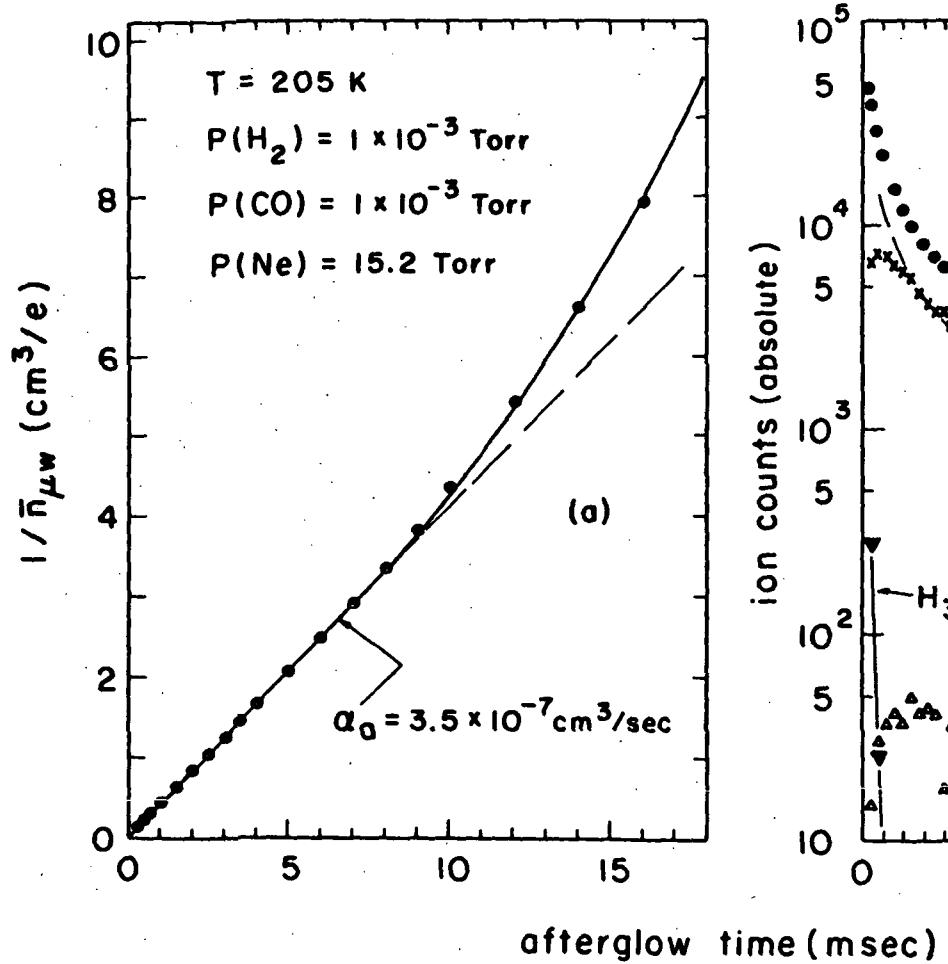


Figure 2